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PAPERS FROM THE PHYSICAL LABORATORIES

No. 18: A METHOD OF DETERMINING THE SPECIFIC HEAT OF A GAS AT CONSTANT PRESSURE, BY H. F. DAWES

(Reprinted from Transactions of the Royal Society of Canada, 1906)

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XII.—*A Method of Determining the Specific Heat of a Gas at Constant Pressure.*

By H. F. DAWES, M.A., University of Toronto.

(Communicated by Prof. J. C. McLennan, and read May 23, 1906.)

The classical determination of this constant for several gases was made by Regnault.[1] His method consisted in passing a stream of heated gas through an ordinary water calorimeter and determining the quantity of heat given up by observing the rise in temperature of the water. The quantity of gas used in any experiment was determined from observations on the pressure, and the temperature of the gas together with the volume of the reservoir in which it was stored. The gas was heated by passing it through a long spiral tube of copper immersed in a bath of boiling oil. From the heating bath it passed directly into the calorimeter traversing it in a spiral copper tube. It was assumed that the air entered the calorimeter at the temperature of the oil bath, and left it at the temperature of the water.

Besides the heat given up by the gas a certain amount was communicated to the calorimeter by conduction and by radiation both from the bath and from other bodies in the room. In order to determine the amount of heat derived from these sources observations were made on the temperature of the calorimeter for a certain time before the gas was allowed to pass through and again after the flow was stopped.

Defects.

In attempting to repeat this experiment with apparatus precisely similar to that used by Regnault it was found that the arrangement had several disadvantages. In the first place the calorimeter used was not very delicate, *i.e.*, it required a comparatively large quantity of heat to make a sufficiently great difference between the initial and final temperatures of the calorimeter.

Since both the specific heat and the density of a gas are very small, it is necessary to use a large quantity of gas and to make the initial temperature very high in order to have the required quantity of heat available. To obtain a sufficiently high temperature, boiling oil was used in the heating bath and this made the experiment very disagreeable and difficult to work with.

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[1] Regnault. Memoires de l'Academie des Sciences de l'Institut Imperial de France. Tome XXVI. pp. 1-112.

Again, with Regnault's apparatus, the arrangement for measuring the initial temperature of the gas was somewhat defective. On account of the very rapid fall of temperature along the tube through which the gas passed from the oil bath to the calorimeter it was scarcely permissable to assume that it entered the calorimeter at the temperature of the oil bath.

II.—*The Bunsen Ice Calorimeter.*

A modified form of the calorimeter used by Regnault for the determination of the specific heat of gases is also used to find the specific heat of liquids or solids. Another form of calorimeter which has been used for liquids and solids but not for gases is the Bunsen Ice Calorimeter. The construction of this type of calorimeter is shewn diagrammatically in Fig. 1. A glass test tube B is sealed into the upper end of a larger cylindrical glass vessel A. The lower end of A is joined to a U tube AC which carries a cup C at its upper end. A hollow stopper furnished with a three way tap D prolonged into a graduated capillary tube E is fitted into this end. By means of this tap communication can be made from the cup D, which the stopper carries, either to C or to E or from C to E.

In setting up the instrument for use the upper part of A was filled with pure distilled water free from air, and lower part of A, the tube C and part of the capillary with pure boiled mercury. By means of the tap D the end of the mercury thread could be moved to any selected position.

A part of the water in A was frozen and formed into a cap of ice around the immersed part of B as indicated in the diagram. In making all measurements, A, B, and the lower part of C were kept surrounded by ice in order to maintain the apparatus at zero temperature.

The measurement of heat by this calorimeter depends on the fact that water changes its volume on solidifying. If a quantity of heat is communicated through B to the water in A a certain quantity of ice will be melted. This will cause a diminution in the volume of the contents of A, and a consequent receding of the mercury thread in E. From the known values of the latent heat and the specific gravity of ice, the amount of heat communicated may be determined for any change of volume produced.

An investigation with this type of calorimeter shewed that its delicacy was such that an addition of one calorie made a change of about 1 1-3 millimeter divisions in the position of the end of the capillary thread. With the apparatus used by Regnault, on the other hand, an addition of about 600 calories was required to make a difference of one degree in the thermometer reading. Besides its greater sensitiveness the Bunsen calorimeter possesses the advantage of not requiring any correction for radiation errors since no heat is communicated by this means on account of the surrounding ice jacket.

III.—New Method.

A.—*Apparatus.*

In the experiment described below a method was devised by which this calorimeter could be used with special advantage in determining the specific heat of a gas, and at the same time some of the defects of the Regnault arrangement avoided. Fig. 2 is a diagram of the arrangement of the apparatus as finally adopted after considerable development. The gas was stored under pressure in a reservoir A and kept at zero temperature by means of ice in the vessel surrounding it. The flow of gas was regulated by a valve B, and its pressure was indicated by a water manometer C. A phosphoric pentoxide drying tube D was inserted in its path to absorb any moisture coming from the manometer. The gas was heated as it passed through a tube in a water bath E and was kept at a temperature of 100° as far as the mouth of the calorimeter by means of a steam jacket. It passed through the test tube of the calorimeter F in a copper tube of special construction shewn on a larger scale in Fig. 3 The gas entered this tube through the inlet *d* and issued from it by the outlets *a* and *b*, each of which could be closed by a valve. The lower part of the tubing was coiled, as shewn in the figure, and immersed in water to the height *e*. With the valve *b* open and *a* closed the gas passed directly out without going through the bent portion of the tube. The difference of temperature between the points *c*, *d*, was measured by means of a copper-iron thermocouple, the wires of which passed out through air-tight caps at *a* and *b*, and thence to a galvanometer.

B.—Calibration.

(1) *The Thermocouple.*

The thermocouple was calibrated before the wires were sealed into the tubes, one junction being kept in melting ice and the other placed in a water bath along with a standard thermometer. The deflections of the galvanometer were observed for a series of different temperatures, and the results are shown in Fig. 4.

(2) *The Gauge.*

The relation between the quantity of gas which passed out of the reservoir and the corresponding fall of pressure was found in the following way. The volume of the reservoir was 7 litres, so that it contained 7 m grams of gas at standard temperature and pressure, m being the mass of one litre. Hence by Boyle's Law, for every millimetre fall of pressure 7m/760 grams of gas must have escaped. The calibration of the gauge was checked by means of a mercury manometer, and its readings reduced to millimeters of mercury. In an experiment with atmospheric air for which m=1.293 the quantity of air which issued from the reservoir was calculated for a series of different pressure falls and the results of this calculation are exhibited in Fig. 5. In this figure the ordinates represent the quantities of air which escaped when the pressure fell to zero from the values indicated by the corresponding abscissæ.

(3) *The Calorimeter.*

The bore of the capillary tube of the calorimeter was calibrated by filling it with mercury and then running it out a little at a time and weighing the parts run out. From this the mass of mercury occupying each division was found for different parts of the tube.

The number of calories required to cause a displacement of one gram was found as follows:—

Data:—

1 gram of water gives out 80.025 calories on freezing.
1 gram of water occupies 1.00013 c.c at 0°C.
1 gram of ice occupies 1.090 x 1.00013 c.c at 0°C
1 gram of mercury occupies .073553 c.c at 0°C.

Solution:—

80.025 calories used in melting ice cause a change in volume of $1.00013 \left\{ 1.090 - 1 \right\}$ c.c. and therefore cause a displacement of

$$1.00013 \left\{ 1.090 - 1 \right\} \times \frac{1}{.073553} \text{ grams of mercury.}$$

Hence a displacement of one gram of mercury means the using of

$$\frac{.073553 \times 80.025}{1.00013\ (1.090 - 1)} \text{ calories} = 65.4 \text{ calories.}$$

From this value the number of calories causing a displacement of one division at different parts of the scale was found. The results of this calibration are illustrated by Fig 6, which shows at any point the number of calories corresponding to a displacement of the mercury from zero of the scale to that point.

A preliminary experiment showed that the fall of pressure of the gas in passing through the calorimeter was less than one fifth the pressure indicated by the manometer C.

C. Method of Experiment.

In making a determination the following procedure was adopted. When the water in E had been raised to the boiling point the valve *a* was opened, and the gas allowed to pass through the apparatus. Readings were taken on the calorimeter scale, and on the gauge and on the thermocouple scale respectively once a minute. B was adjusted as required to keep the gas flowing uniformly. The water manometer C was maintained at a difference of level of eight millimeters, so that the fall in pressure of the gas as it passed through the calorimeter was less than 8/5 millimeters of water. The galvanometer in a few minutes assumed a constant deflection, showing that the temperature of the *d* junction had become steady. From the calorimeter readings the average number of divisions per minute was determined by finding, first, the average number per twenty minutes from a number of sets of readings, and then taking one twentieth of that number. The rate of fall of pressure was found in a similar manner from the readings of the gauge.

After the gas had been flowing for a sufficient time, the valve *b* was opened and *a* closed, so that the gas passed out without going through the coil. The rate of flow was adjusted so that the thermocouple *d* was kept at a temperature used in the previous observations. Readings of the calorimeter and of the thermocouple scales were taken once a minute as before, and the average number of divisions per minute on the calorimeter scale was found in the way explained above.

From these readings the following deductions were made:—

(1) The temperature in degrees centigrade corresponding to the thermocouple deflection was found from the curve of Fig. 4.

(2) The number of grams of gas per minute was found from the rate of fall of the pressure by means of curve 5.

(3) By the aid of curve 6 the number of calories communicated per minute to the calorimeter was deduced from the number of divisions moved over per minute by the mercury thread.

D. Theory.

It will be seen that with the exception of the air which passed through the coil (*e*) during the first set of observations the sources of heat in the two cases were exactly the same. Hence if "x" calories per minute were communicated in the first case, and ("x_0") per minute in the second, the gas must have given up $(x - x_0)$ calories per minute. If therefore the rate of flow was "y" grams per minute, and the fall of temperature "t°C" the value of the specific heat as given by this set of readings was $\frac{x - x_0}{yt}$

E. Measurement of Specific Heat for Dry Air.

A set of temperature, pressure, and calorimetric readings for dry air is given in Table I, and curves illustrating them are shewn in Fig. 7.

TABLE I.

Time.	Gauge.	Time.	Calorimeter Scale.	Thermocouple Scale.
0.	22.9	....	....	....
.30	22.7	1	554.4	....
1.30	22.1	2	560.3	65.5
2.30	21.6	3	566.4	65.
3.30	21.3	4	572.9	64.5
4.30	20.9	5	579.	64.5
5.30	20.6	6	585.1	64.
6.30	20.1	7	591.8	64.5
7.30	19.9	8	598.	64.5
8.30	19.55	9	604.1	64.5
9.30	19.2	10	610.3	64.5
10.30	18.9	11	617.	64.5
11.30	18.6	12	623	64.5
12.30	18.5	13	629.9	64.5
13.30	18.2	14	636	64.5
14.30	18.	15	642.4	64.5
15.30	17.5	16	649	64.5
16.30	17.1	17	655.2	64.5
17.30	16.7	18	661.8	64.5
18.30	16.4	19	668.5	64.5
19.30	16.2	20	675.0	64.5

TABLE I—(*Continued.*)

Time.	Gauge.	Time.	Calorimeter Scale.	Thermocouple Scale.
20.30	15.8	21	681.6	64.5
21.30	15.1	22	688.2	64.5
22.30	15.	23	694.9	64.5
23.30	14.6	24	701.3	64.5
24.30	14.2	25	708.	64.5
25.30	14.	26	715	64.5
26.30	13.6	27	721.3	64.5
27.30	13.3	28	728	64.5
28.30	12.95	29	734.9	64.5
29.30	12.4	30	741.5	64.5
30.30	12.	31	748.5	64.5
31.30	11.6	32	755	64.5
32.30	11.4	33	762	64.5
33.30	11.	34	769	64.5
34.30	10.7	35	775.4	64.5
35.30	....	36	782	64.5
36.30	10.35	37	789.1	64.5

The first of these curves (A) shews that after the first few minutes the temperature became steady and remained so during the experiment. The scond and third (B and C), shew respectively that the air flowed through the calorimeter uniformly, and that the heat was communicated to it at a uniform rate.

The determination of the value of the specific heat at constant pressure for air from this set of readings is summed up in the following:

Denoting the rate of motion of the calorimeter thread when the air was flowing through the coil by A, and when it was issuing from the outlet *b* by B, the results obtained were as follows:—

Average value of A = 6.612 divisions per minute.
Temperature fall between terminals of thermocouple = 21.9°
Average value of B = 4.982 divisions per minute.
Temperature fall = 21.8°
Reduced value of B corresponding to temperature fall of 21.9° = 5.0071 divisions per minute.

.—Calorimeter scale divisions due to the heat from the air = (6.612 - 5.0071) = 1.6049. From Fig. 7 and its corresponding readings the number of calories per minute due to the heat imparted by the air = 1.20027.

II.—Average fall of pressure = .3399 gauge divisions per minute, = 17.09 mm. mercury per minute and consequently the average rate of flow = .20355 grams per minute.

Combining I and II the value .2697 was obtained for the specific heat at constant pressure.

F. Discussion.

In the published account of the experiments in which he determined this constant. Regnault gives the results of eight-four determinations. These vary from .22 to .24 the average value being .2375. The result found from the observations given above, while somewhat higher than those found by Regnault is still sufficiently near to his values to demonstrate the usefulness of the method.

G. Alterations Suggested.

One or two changes in the arrangement have suggested themselves, but owing to lack of time, have not as yet been tried. In the first place the junction of the two tubes at *d* might be made quite near to the upper end of the test tube of the calorimeter, and the thermojunction moved up to correspond. This would not alter "x" as used in the above discussion, but would make a much greater value of "t" and a correspondingly smaller value of "x_0" since the heat given up by the air between the present position of *d* and that suggested is at present included in "x_0." Again, an ebonite connection in the tube *d* would lessen the conduction from the steam jacket, ebonite being a poor conductor of heat. This would lessen the values of "x" and "x_0" by equal amounts. Both these changes would lessen the percentage error in the final result.

H. Advantages of the Method.

Some advantages of this method over that used by Regnault may be enumerated.

(1) By this method the calorimetry is more perfect than in the experiments of Regnault, since the calorimeter (a) is very much more sensitive and (b) it requires no correction for radiation on account of belonging to the constant temperature type.

(2) Heat communicated by all sources other than the gas itself, for example, by conduction from the steam jacket down the tube, *d*, and from the air of the room down *a* and *b*, is accounted for by a single direct observation.

(3) Again, in this method the measurement of the initial temperature of the gas is exact, since all heat given up by it after it passes the thermocouple is accounted for in the calorimeter readings.

(4) It is necessary to heat the gas only to a comparatively low temperature in order to have as favourable a determination as that of Regnault with the very high temperatures he used. Hence the disadvantages and limitations of using boiling oil as a heating bath are avoided. The method may be readily applied to gases which are decomposed at high temperatures.

(5) The determination of the specific heat of a gas is reduced to the measurement of rates, so that the initial and final adjustments of conditions have not to be considered or allowed for.

(6) The method may be readily adapted to the measurement of the specific heat of liquids so that it gives promise of becoming generally useful.

The writer would in conclusion express his sincere thanks to Prof. J. C. McLennan for his kindly interest in this investigation, and his helpful suggestions during its progress.

Physical Laboratory, University of Toronto.

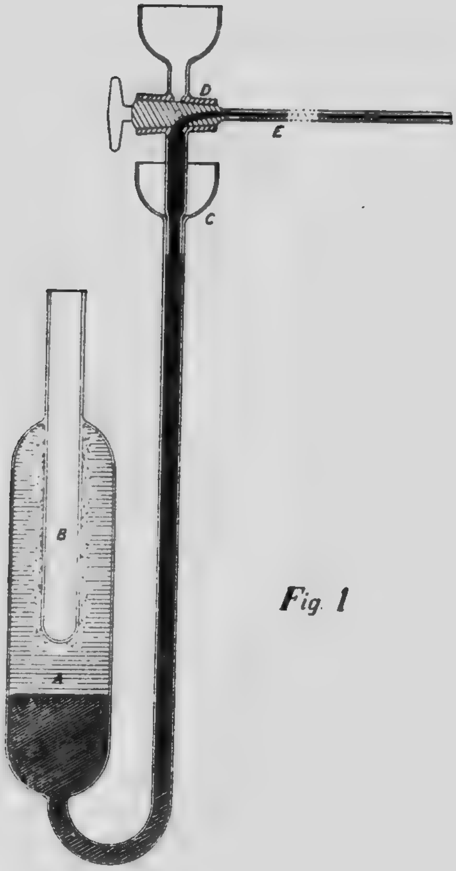


Fig. 1

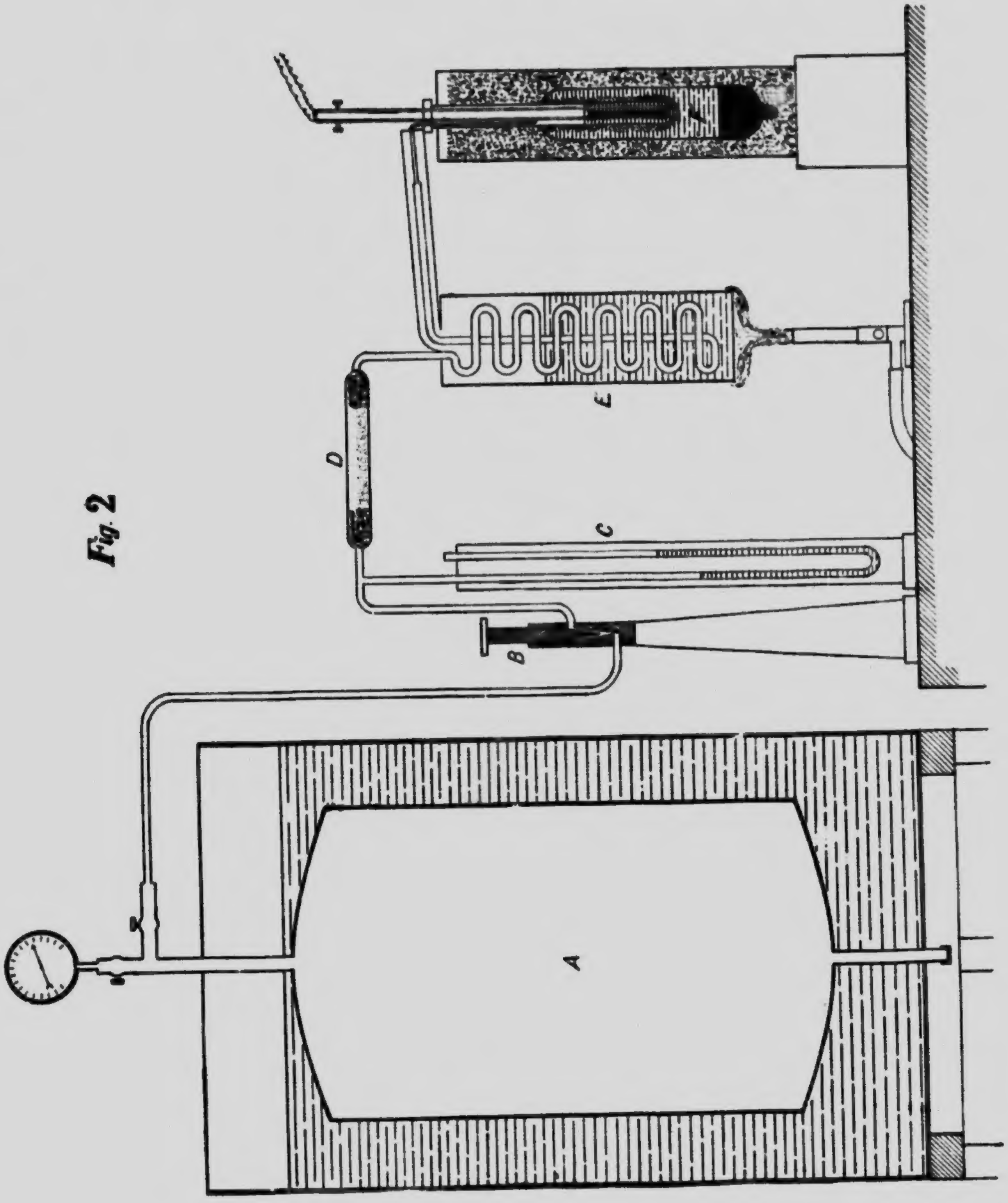
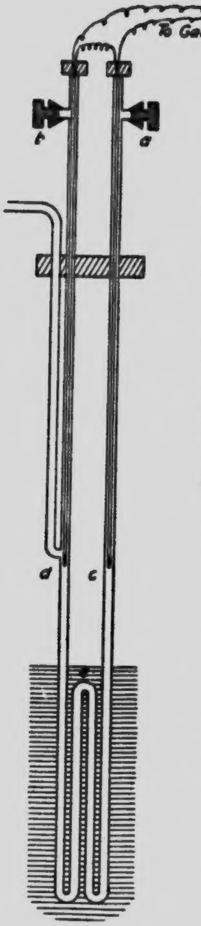


Fig. 2

Fig. 3



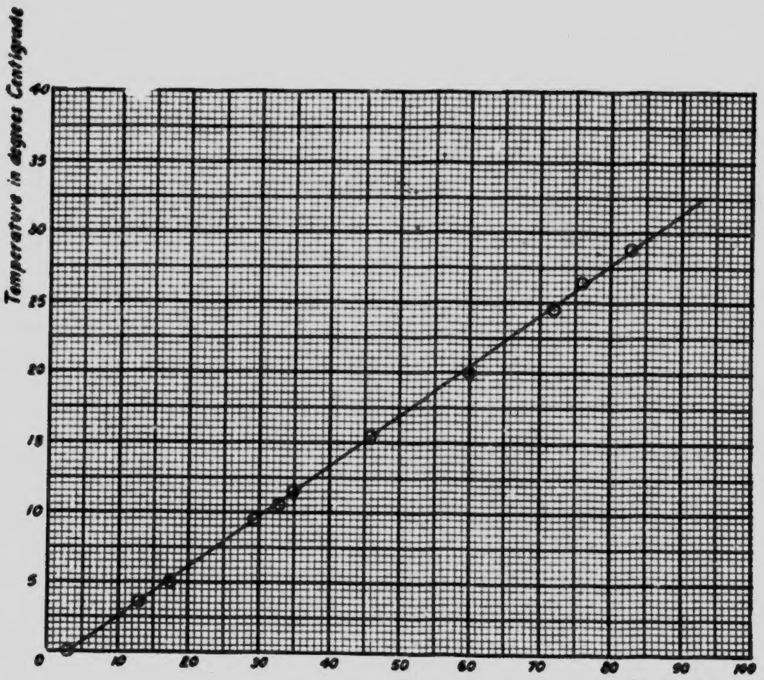


Fig 4
Calibration of Thermocouple

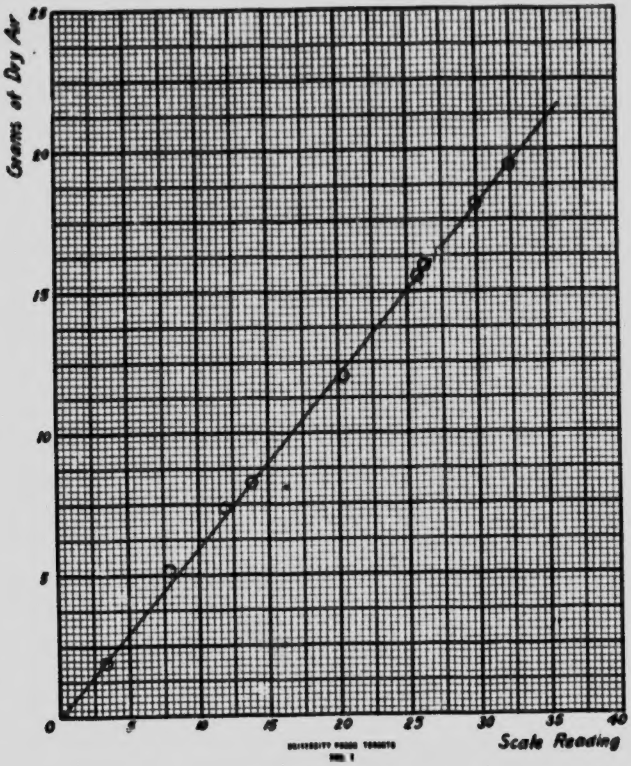


Fig 5
Calibration of Gauge

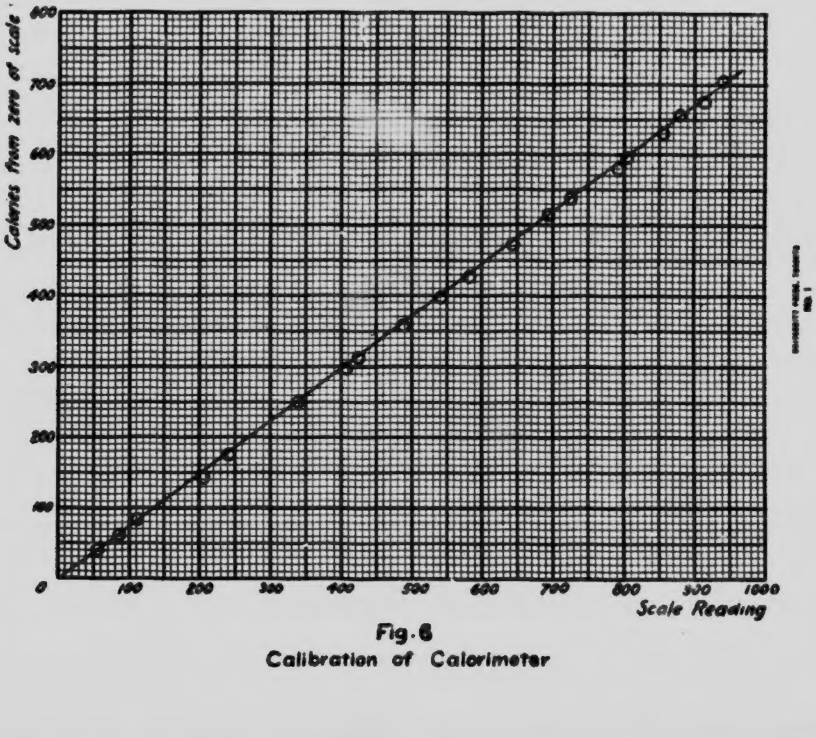


Fig. 6
Calibration of Calorimeter

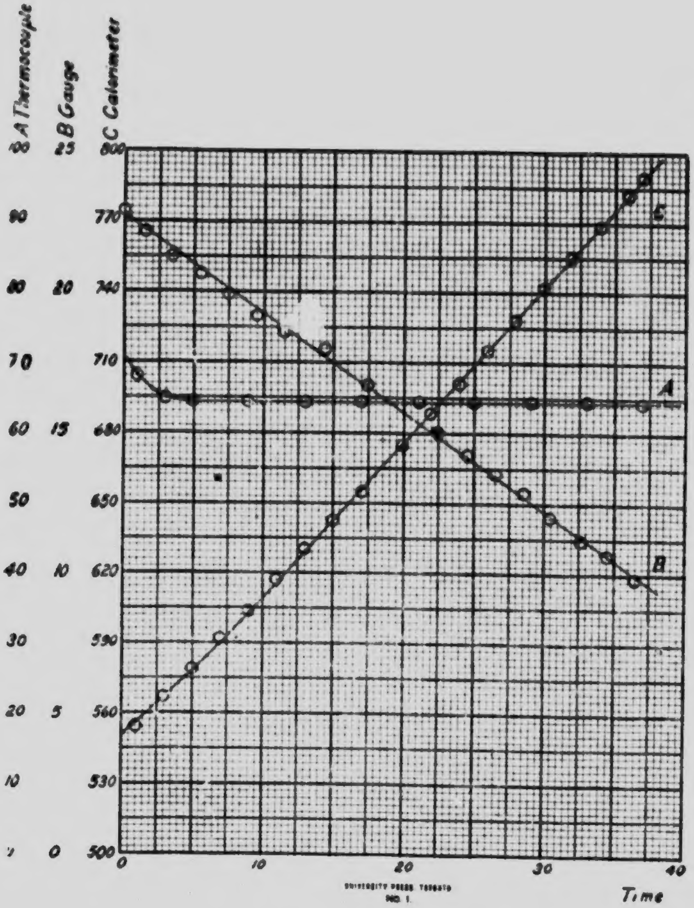


Fig. 7

A Readings of Thermocouple
B " " Gauge
C " " Calorimeter